

LA-UR-16-21702 (Accepted Manuscript)

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Provided by the author(s) and the Los Alamos National Laboratory (2016-10-20).

To be published in: MRS Advances

DOI to publisher's version: 10.1557/adv.2016.353

Permalink to record: <http://permalink.lanl.gov/object/view?what=info:lanl-repo/lareport/LA-UR-16-21702>

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MRS Advances / *FirstView* Article / May 2016, pp 1 - 7
DOI: 10.1557/adv.2016.353, Published online: 16 May 2016

Link to this article: http://journals.cambridge.org/abstract_S2059852116003534

How to cite this article:

Jamie L. Doyle, Daniel Schwartz and Lav Tandon Nuclear Forensics of a Non-Traditional Sample: Neptunium. MRS Advances, Available on CJO 2016 doi:10.1557/adv.2016.353

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ABSTRACT

Recent nuclear forensics cases have focused primarily on plutonium (Pu) and uranium (U) materials. By definition however, nuclear forensics can apply to any diverted nuclear material. This includes neptunium (Np), an internationally safeguarded material like Pu and U, that could offer a nuclear security concern if significant quantities were found outside of regulatory control. This case study couples scanning electron microscopy (SEM) with quantitative analysis using newly developed specialized software, to evaluate a non-traditional nuclear forensic sample of Np. The results of the morphological analyses were compared with another Np sample of known pedigree, as well as other traditional actinide materials in order to determine potential processing and point-of-origin.

INTRODUCTION

The use of scanning electron microscopy (SEM) for nuclear forensic analysis has become quite common as SEM offers several advantages to sample characterization[1, 2]. The technique provides superior resolution (compared to optical microscopy), is fundamentally non-destructive, requires minimal sample preparation, and can be combined with x-ray analysis for direct elemental characterization[3]. When applied to nuclear forensic samples, scientists can use the high resolution images to correlate the morphological features with potential processing signatures[4]. Variations in processing and precipitation conditions have been observed to influence the final material morphology, thus providing a forensic signature[5]. Morphological attributes, as they pertain to nuclear forensics, are only beginning to be evaluated[6].

The prevalence of nuclear material morphology in literature is growing, but with a strong emphasis towards plutonium (Pu) and uranium (U) morphologies[2, 4, 5, 7-13]. Although Pu and U are the most common interdicted nuclear material cases, other safeguarded materials, like neptunium (Np), also have the potential to appear in forensic cases[14-16]. Morphological analysis of Np is much less common in the literature than Pu and U, the main sources of Np morphology being reports from Savannah River National Laboratory (SRNL) investigating the optimal production and stabilizing conditions for $^{237}\text{NpO}_2$ targets[17-20].

This study focuses on the morphological features of two $^{237}\text{NpO}_2$ materials: one of an unknown origin and the other a material of known pedigree. In addition to traditional qualitative analysis, SEM images of both samples were evaluated quantitatively using specialized software developed at Los Alamos National Laboratory. The measured/observed features of these materials were then compared with older morphological studies of NpO_2 as well as Pu and U oxides to help determine the possible processing conditions and point-of-origin of the unknown.

EXPERIMENTAL DETAILS

Both $^{237}\text{NpO}_2$ specimens were mounted by dispersing a few milligrams of each material onto a conductive carbon sticky tape applied to a standard SEM “tee” mount. After loading, using a

sharp-tipped, flat spatula, the specimens were tapped to remove loose material and transferred to a sputter coater to apply a thin gold (Au) film. Prepared samples were analyzed using a FEI Quanta 250 SEM (FEI, Hillsboro, OR).

DISCUSSION

The known material originated from an impure NpO_2 material at Los Alamos National Laboratory (LANL) which was derived from Np metal. The oxide was dissolved and precipitated as a peroxide following a method developed by Burney and Dukes to remove elemental impurities such as iron (Fe)[21, 22]. The precipitate was re-dissolved in HCl and further purification by anion exchange (Reillex HPQ anion exchange resin). Finally, the oxidation state of the purified Np was adjusted with hydroxylamine hydrochloride and precipitated as Np(IV) oxalate. The precipitate was then calcined at 200°C, 400°C, 600°C, and 950°C for 2 hours each to produce the final $^{237}\text{NpO}_2$ material[22].

The known material when inspected via SEM had relatively amorphous features and a wide range of particle sizes and shapes. Fines ($< 5 \mu\text{m}$) could be seen at higher magnifications as well as a number of distinctly unique surface features. Figure 1 shows SEM images of the known at varying magnifications. The particles could be described as irregular, weak agglomerates; they appeared to be somewhat angular with sub-rounded features. Upon closer examination of the surfaces, slight heterogeneity in the morphology could be observed. Figure 1B shows the “typical” particle surface for the material, apparently rough, layered, porous, and generally irregular. Figure 1C and 1D show other more unique features found on the surface of specific particles. Figure 1C highlights an uncommon but distinctive surface feature which appeared to be smoothed, layered, and striated in a specific direction, while Figure 1D shows the lumpy, globular feature that appeared with more frequency on several of the particles.

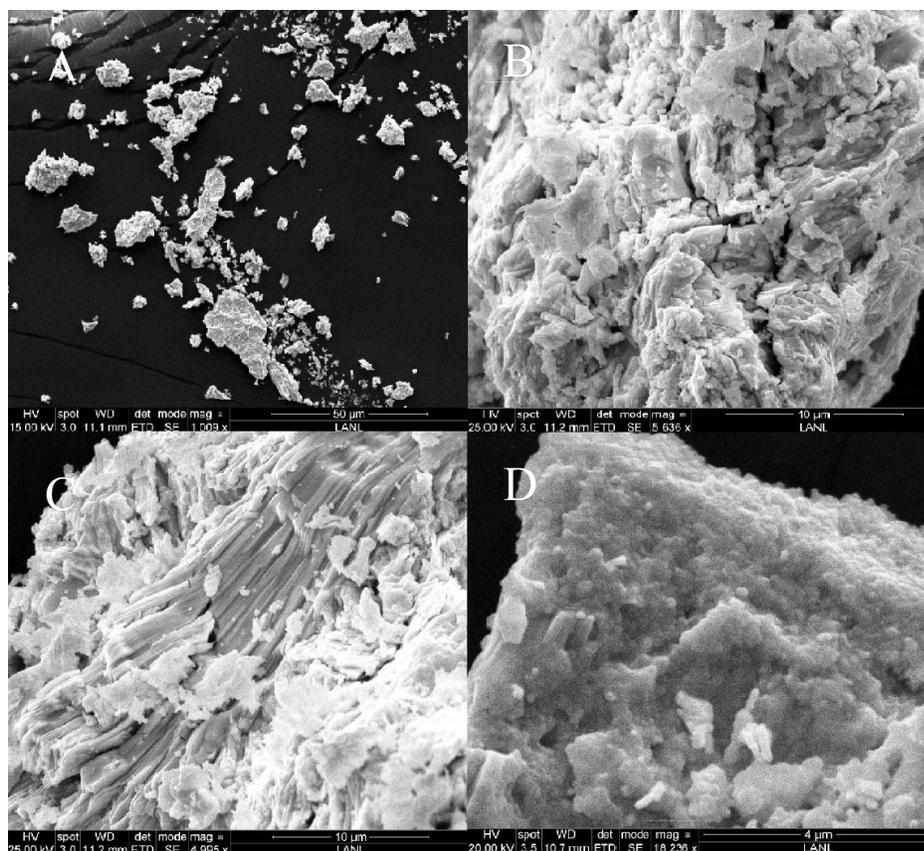


Figure 1. SEM images of the known NpO_2 material. A) Multiple particles of the known, size bar in lower right corner at $50\mu\text{m}$. B) Single particle surface, $10\mu\text{m}$ size bar. C) Single particle feature, $10\mu\text{m}$ size bar. D) Single particle feature, $4\mu\text{m}$ size bar.

NpO_2 morphology has been documented to change as a function primarily of precipitation conditions and calcination temperature[17, 19]. The observed morphology of the known can be correlated to the particular processes described in the production documentation. First, the material does not appear to have any defined structure. This lack of structure provides evidence that the NpO_2 was not likely to have been produced via typical oxalate precipitation methods, such as those historically used at SRNL. The SRNL methods produced larger, more ordered, and uniform particles, with the exact shape and dimensions resulting from the precipitation conditions used[18]. Besides differences in material purification steps, HCl was documented as the primary precipitation matrix in the known production process. HNO_3 is typically used as the primary matrix in historical oxalate precipitations. This significant deviation in the process could explain notable differences observed in the known material morphology as compared to the morphology obtained by historic methods. Additionally, the lumpy, globular surface features observed, can be correlated to the calcination. Calcination temperatures greater than $> 800^\circ\text{C}$ have been observed to yield this morphology, as seen with U oxides[12]. Therefore, it was evident that this material was calcined at a temperature equal to or greater than 800°C . The documented production method confirms this observation as well.

Quantitative analysis of the average particle area, perimeter, circularity, and other features can provide further comparators to hypothesize production process. Using the Morphological Analysis for Materials Attribution (MAMA) Software (Table I) developed at LANL, several

quantitative particle measures were made and compared between the known and unknown materials. This specialized software allows non-experts to quickly, easily, objectively, and quantitatively analyze an image for size, shape, and morphological features[11]. By incorporating expert knowledge and a representative lexicon, accurate, consistent, and robust interpretations of an image can be achieved for nuclear forensic investigations. The smaller area and equivalent circular diameter (ECD) observed for the known material can be correlated with the documented atypical precipitation and calcination (Table I). Higher calcination temperatures generally reduce the overall particle size, while the alternative precipitation approach can be related to the irregular particle shape (low EDC, ellipse perimeter, etc.) [23, 24].

Table I. Comparison of several quantitative features with the standard associated error in parenthesis of the known and unknown samples.

	Count (particles)	Pixel Area (μm^2)	ECD (μm)	Ellipse Perimeter (μm)	Diameter Aspect Ratio	Circularity
Known	740	39.34 (7.10)	4.41 (0.20)	15.93 (0.79)	1.75 (0.02)	0.59 (0.01)
Unknown	339	251.28 (9.26)	17.04 (0.30)	57.52 (1.02)	1.38 (0.01)	0.55 (0.00)

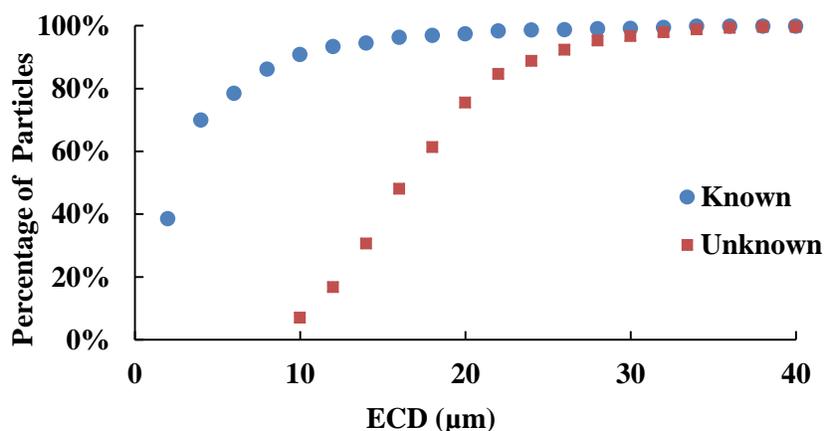


Figure 2. Cumulative distribution plot of ECD for each material, blue corresponding to the known material and red to the unknown. For the known material, only particles with ECD > 1 μm were counted, and for the unknown material ECD > 8 μm .

Quantitative analysis of the unknown NpO_2 (form visually assessed as NpO_2 from the light brown-green color of the bulk powder) showed the particles were much larger with a more defined shape than the known material (Table I, Figure 2)[25, 26]. Figure 2 compares the distribution of ECD or size for the two materials. Approximately 50% of the unknown particles are about 15-16 μm or greater in ECD, while almost 95% of the known particles are 15-16 μm or less. Both materials however, do not typically show particles greater than 35 μm ECD. These quantitative measures could be confirmed visually in the SEM images (Figure 3). The unknown NpO_2 showed highly crystalline, agglomerated particles. In general, the particles were

somewhat round with a more uniform shape as can be discerned in Figure 3A and confirmed by MAMA (Table I)[27, 28].

Magnification of these rounded particles showed the surface was more uniform, as equiaxed, cuboidal layers, than those observed in the known material. Referencing published morphological studies of NpO_2 , this structure was more typical[17-20]. As previously discussed, SRNL oxalate precipitation showed similar characteristics, i.e. NpO_2 particles with a rosette morphology and layered, equiaxed cuboidal features[19]. However, certain conditions can be ruled out based on structure. For example, it was unlikely the precipitation was completed at temperatures higher or lower than 50°C as morphologies associated with these temperatures showed significant variations in agglomeration and did not typically match the structure observed in Figure 3[19]. Precipitation temperature however, was just one of many factors that could affect the structure. Changes in precipitation method (direct vs. reverse strike), HNO_3 concentration, Np concentration, oxalate concentration, reductant concentration, and addition/processing rates, etc. could all influence the morphological features observed[18, 19, 29].

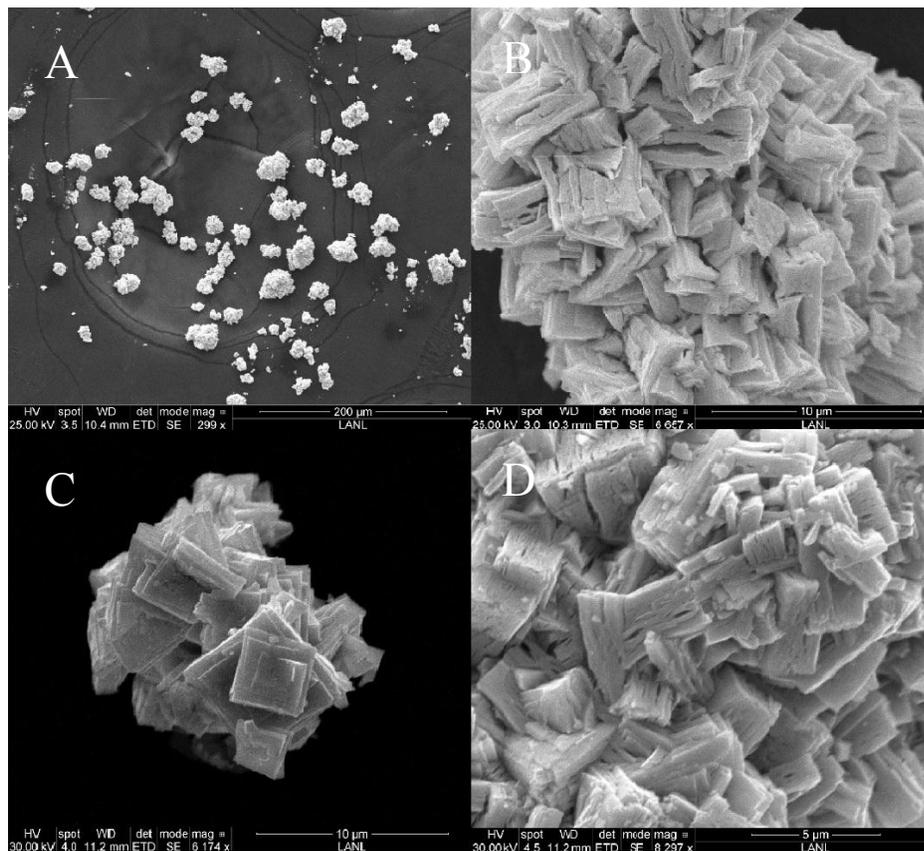


Figure 3. SEM images of the unknown NpO_2 material. A) Multiple particles of the unknown, size bar in lower right corner at $200\ \mu\text{m}$. B) Single particle surface, $10\ \mu\text{m}$ size bar. C) Single particle, $10\ \mu\text{m}$ size bar. D) Surface features of a single particle, $5\ \mu\text{m}$ size bar.

The smoother facets of the unknown compared to the known, suggest the material was most likely calcined at temperatures below 800°C . Temperatures of $600\text{--}650^\circ\text{C}$ were most commonly

reported for NpO₂ production processes. Considering the similarities of the unknown material to historical SRNL materials, the unknown was likely to have some relation to SRNL production. One signature of the SRNL process, in addition to morphology, was the presence of aluminum (Al), which was blended into the material during ²³⁷NpO₂ target fabrication for ²³⁸Pu production [18, 19]. Energy Dispersive Spectroscopy (EDS) was used to identify impurities in both samples. The known spectrum, as expected from the documented purification, showed no significant impurity peaks. However the unknown NpO₂ displayed an impurity peak from Al, suggesting the material had been purified, but could not be fully purified from Al. This impurity was detected on the particles selected from the SEM image on a microscale, whereas the full chemical analysis showed the Al content of the bulk was below the limit of detection for the instrument (3 µg/g). This suggests that the Al was not heterogeneously integrated into the material. Considering the alumina was added to the NpO₂ targets as a solid and cold pressed, this heterogeneity would be expected [19]. It appears even more likely the unknown material originated from SRNL. A full forensic analysis of the unknown material was completed using wet chemistry methods and the results of the investigation compliment the results and conclusions reported here [30].

CONCLUSIONS

Processing conditions of the known NpO₂ were observed in the imaged morphological features. In particular, calcination above 800°C and precipitation conditions dissimilar to the SRNL methods were observed to have a direct effect on morphology. Likewise, the morphological analysis of the unknown NpO₂ assisted in forming a potential point-of-origin based on the similarities of the observed material with that historically produced at SRNL. The specifics of each process condition could not be discerned from the SEM analysis alone. The EDS spectra of the material showed it had most likely undergone some separation/purification as it appeared to be relatively pure, with the exception of Al, an elemental impurity signature common to SRNL NpO₂. The structure of the unknown and presence of Al support the hypothesis that the unknown material may have originated from SRNL processing.

ACKNOWLEDGEMENTS

The authors would like to thank Elmer Lujan, Kathy Garduno, and Kevin Kuhn for their help and guidance with this study. The authors would also like to gratefully acknowledge the U.S. DHS/DNDO National Technical Nuclear Forensics Center (HSHQDC-14-X-00028) for funding this work at Los Alamos National Laboratory. This support does not constitute an express or implied endorsement on the part of the Government. This document is LA-UR-16-21702.

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